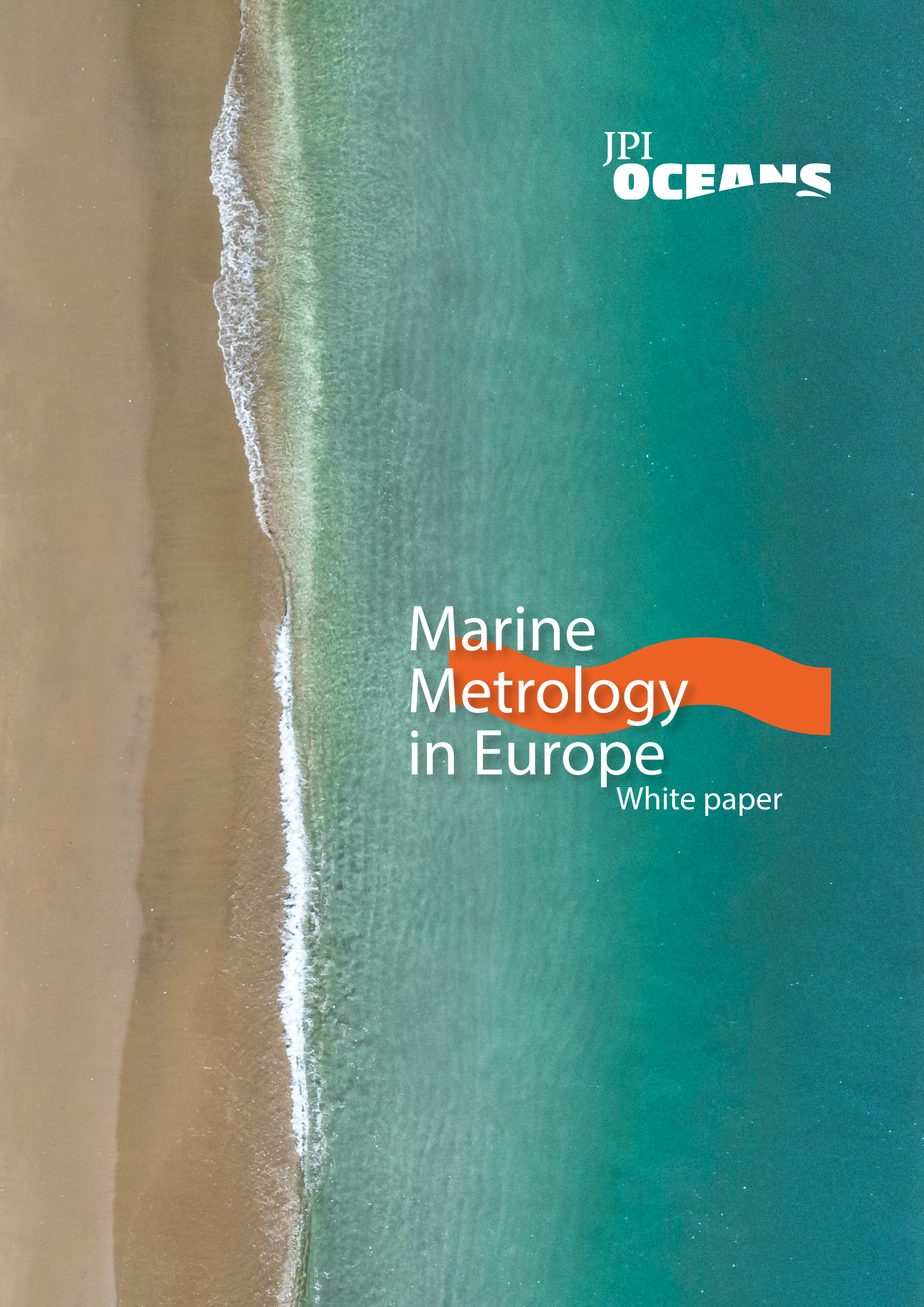

JPI OCEANS

Marine Metrology in Europe

White paper

JPI OCEANS

WHITE PAPER

MARINE METROLOGY IN EUROPE

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Suggested Reference:
JPI Oceans (2021) Marine Metrology in Europe - White Paper. Joint Programming Initiative Healthy and Productive Seas and Oceans, Brussels.
DOI: https://hdl.handle net/10.48470/16

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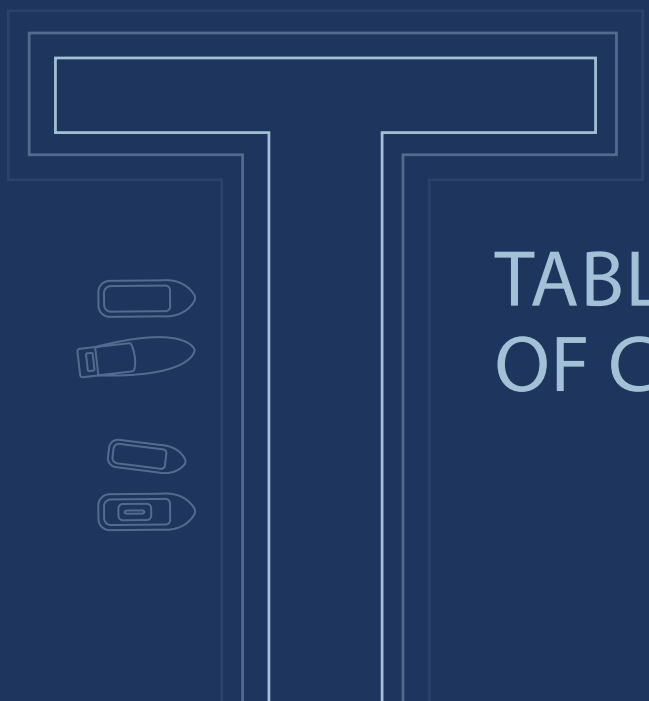

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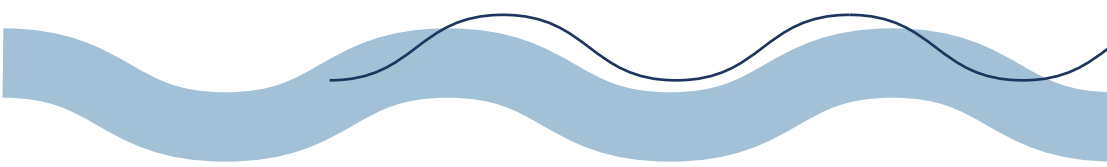
1.0 INTRODUCTION

Europe spends €1.4 billion p.a. for marine data collection: €0.4 billion for satellite data and €1.0 billion for in-situ observations, respectively. In the case of the latter, the traditional and expensive practice of vessel-based data-gathering is progressively giving way to monitoring via "observatories" - complexes of distributed, autonomous, real-time sensor systems.

Burgeoning technology and pressing societal needs will soon make such observatories the backbone of European marine observing activity because of their ability to provide copious quantities of diversified data over large areas at reasonable costs. But to be useful for research and decisionmaking at a transnational level, all the incoming data have to be comparable and amenable to fitness-for-purpose assessments in relation to specific user-group requirements.

This will require measurements to be metrologically referenced, and instruments to be working within known specifications at all times despite prolonged deployment in harsh conditions. Basically, the degree to which these two conditions are realized constitutes the only consistent indicator of the quality of a measurement, and hence, of the validity and value of any resulting data.

The standard data quality checks employed by marine data management infrastructures generally relate the "goodness" of data to statistics of the underlying databases and not to actual physical references. The only realistic way to achieve these goals will be through continuous, responsive, high-quality calibrating activity. Calibration, unlike validation, which can be performed with various ways and methods, requires standardized techniques, specialized equipment and skilled operators.



2.0 BACKGROUND

The main stakeholder groups in the marine environmental monitoring and calibration value chain are:

- **Sensor developers and manufacturers;**
- **National Metrological Institutes;**
- **Metrology services of oceanographic Institutes;**
- **Monitoring service providers;**
- **Users of data.**

The marine sensor market is a growing one. There is a constant call for development of new sensor products that can measure additional parameters, meet with stricter requirements and have lower purchase and maintenance costs. Therefore, a large amount of resources (relative to the market size) is applied in research to further develop new or existing sensors still. Highly specialised scientists are required to perform the research necessary to keep up with this flourishing market and its increasing demands. The focus of sensor development can be both cost reduction as well as product diversification, i.e. by building more robust and reliable versions of existing sensors or producing sensors capable of measuring additional parameters (or provide more detailed measurements).

The increasing amount of measured parameters, technologies and, finally, data collected, requires the development of an appropriate and sustainable metrological framework. However, the absence of reference material and/or standard procedures and equipment, especially for new parameters, is a significant problem often faced in the above endeavour.

National Metrological Institutes (NMIs) have a mandate to ensure a continuously functioning, and consequently, a reliable and progressive metrological infrastructure which meets both the highest requirements of science and high-tech industry, on the one hand, and the marginal conditions of legal metrology in everyday life, on the other. The activities of the NMI's include among others:

Research and Technology Transfer:

creating standards, developing new measurement and test methods and furthering standardization, directly benefitting companies and the international metrology community through ever more accurate measurements – the vectors of innovation.

Calibration, tests, analysis: services to companies – calibration and tests covering a wide range of quantities and technologies – to enable them to guarantee the traceability of their measurements and monitor their production quality.

Technical assistance: information on standards and regulations, performance of audits and diagnoses, preparation of manufacturers' specifications, development oftest benches: tailor-made responses to specific measurement problems of companies.

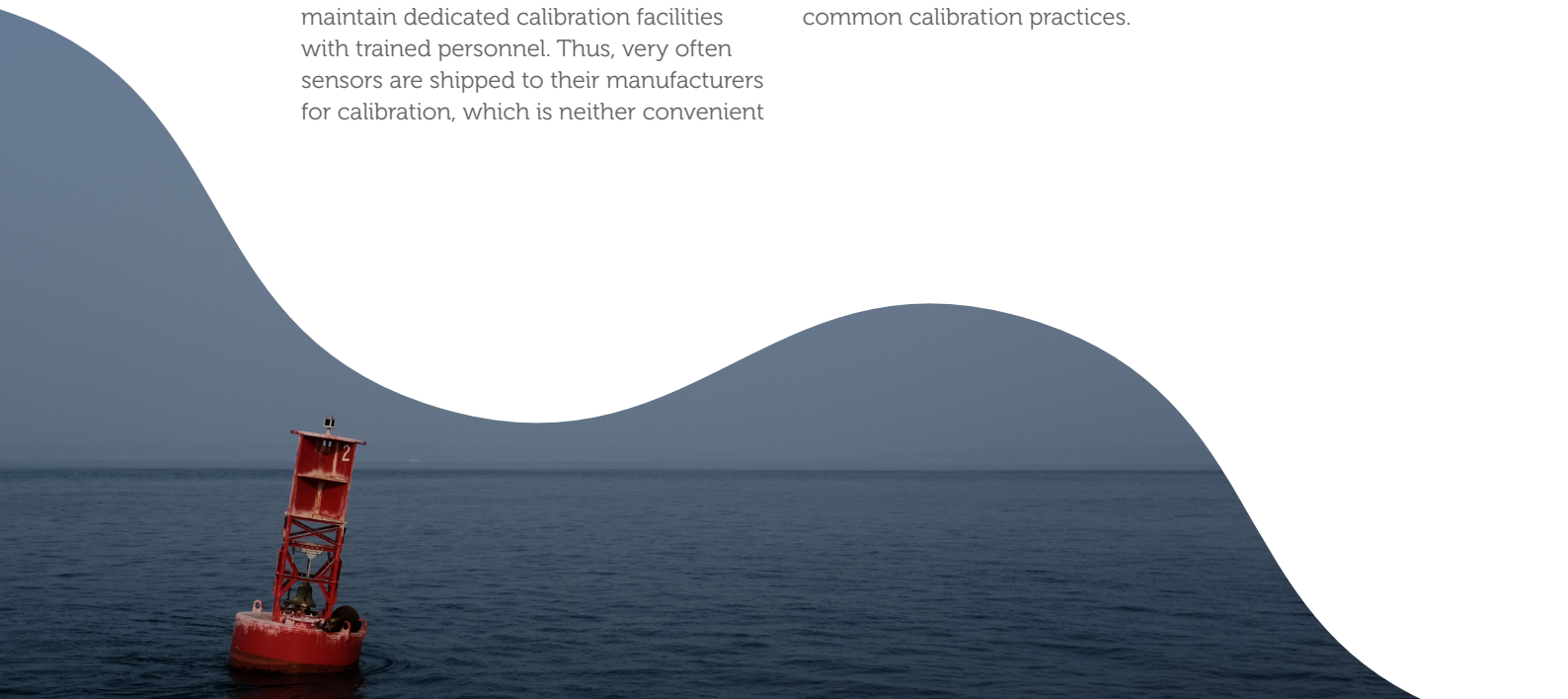
Certification: one-stop solution for voluntary or statutory certification of products,management systems and services, enabling companies to enhance their products in markets worldwide.

Training and information: training sessions, information days on standards and regulations, online metrology training and online publications providing companies with access to up-to-the-minute information on new technology and regulations.

The role of metrology services of oceanographic institutes is to calibrate the big number of devices used during campaigns at sea and on mooring facilities, with instruments referenced to NMI's, when traceability to the International System of Units exits for the oceanographic measured quantities. They calibrate sensors also for inter-organism's projects like for example, the French consortium Coriolis, which is a part of the international ARGO project which goal is to maintain at sea 4000 drifting floats. It is also a contribution to the Global Ocean Surface Underway Data (GOSUD) programme, collecting data from a network of vessels equipped with thermo-salinometers used to calibrate and validate satellites observations.

But, as revealed through the JERICO project activities and in particular Deliverable 4.1 "Report on existing calibration facilities", very few marine research and service operators actually maintain dedicated calibration facilities with trained personnel. Thus, very often sensors are shipped to their manufacturers for calibration, which is neither convenient nor cost efficient. Moreover, manufacturers are both the "judges" and the "judged" in this process of qualification, and it is hard for users to really evaluate the reliability of their sensors/instruments and properly plan relevant calibration intervals. The maintenance intervals have to be planned according to the requirements of each sensor (need for double sets of sensors). Thus, transport and calibration costs of sensors and instruments often constitute a major part of the total running costs of any observing infrastructure. Operating calibration facilities often face difficulties in maintaining dedicated personnel and evolving to meet new challenges, as funding is variable and rather insecure. Although there is significant experience among European research institutes on calibration methods, at present a few labs work independently with no or very little connection with other labs.

Without coordinated and commonly agreed calibration practices, the great part of the value of measurements is lost. Data collected and stored in databases, by various institutes and nations, can only be efficiently combined and new information created, if they are measured using properly calibrated sensors. Calibration network is clearly a joint European objective and will increase the value of collected data. The calibration network is timely due to increased emphasis of sharing data (e.g. Copernicus and EMODnet activities) and increased use of biogeochemical sensors, especially lacking common calibration practices.



3.0 PRESENT STATUS

Metrology is the science dedicated to measurement. The process of measurement presupposes a description of the measured quantity as a referenced numerical value commensurate with its intended use. A specified measurement procedure and a calibrated measuring system operating according to that procedure are almost always implied.

A qualified measurement necessitates the implementation of recognized references and a validated calibration procedure, and the measurement result has to be accompanied by an estimate of the associated uncertainty and must be traceable to an agreed metrological reference, preferably to the International System of Units (SI). The traceability of marine measurements to the SI is essential for achieving true inter-comparability of marine data at the transnational level and in the long term.

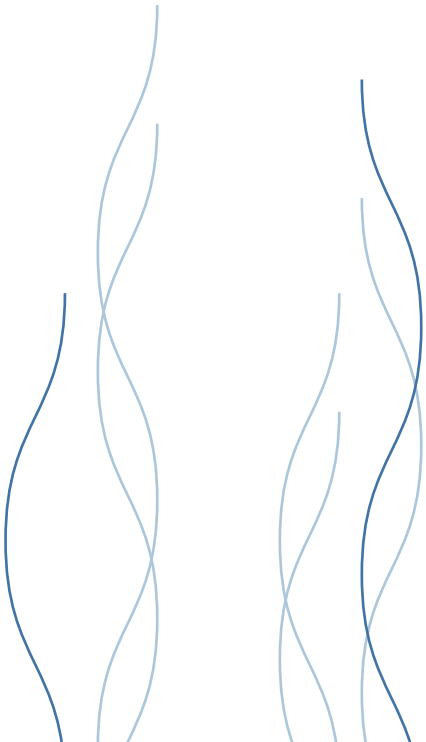
Ensuring traceability will help to:

- relate measurements to recognized, accepted reference material and/or standards;
- estimate effective uncertainties associated with measured data;
- formulate procedures and documentation to handle sensors and data properly;
- harmonize relevant operating practices, particularly those relating to the calibration of instrumentation, on the European scale;
- realistically evaluate the usability and long-term validity of gathered data;
- establish benchmarks for long term comparisons of, and calculation of trends in, measured variables.

The number of the most commonly measured oceanographic parameters is not large - roughly ten or so in addition to the three state variables, pressure, temperature and salinity. Of these, only temperature and pressure measurements are currently formally traceable to the SI, while in the case of all the other variables, procedures to ensure traceability have yet to be established.

However, even for those parameters for which their calibration procedure is generally well defined, there are issues as discussed here, demonstrating the need for a continuous pursue for higher accuracy and lower uncertainty.

Below a mapping of the present status for the key parameters and the challenges are presented in a concise manner.



3.1 TEMPERATURE

Fernando Sparasci

Temperature is a key quantity in marine measurements: it is one of the input terms of the state equation of seawater[1] and is a significant influence quantity impacting the measurement of many marine parameters. It plays a key role in the determination of salinity by conductivity, where it accounts for more than 80%[2] in measurement accuracy.

Temperature is currently defined by the triple point of water and the International Temperature Scale of 1990 (ITS-90). It can be measured with an accuracy better than 0.5 mK only by top-level metrological laboratories (usually NMIs), with specific laboratory equipment.

The target metrological uncertainty for seawater temperature measurements has been set to 2 mK by the WOCE[3] Hydrographic Programme. Recent studies[4] have demonstrated that an accuracy better than 1 mK would be advisable to trace ocean temperature changes below 700 m over several decades. These targets are extremely close to the best measurement capabilities of NMIs. Thus, at least three challenges can be identified in the measurement of seawater temperature:

1. development of procedures to enable in-situ measurements with accuracy better than 2 mK;
2. development of new temperature sensors for seawater;
3. direct measurement of the thermodynamic temperature.

PROCEDURES FOR ACCURATE IN-SITU MEASUREMENTS

Temperature measurements performed in-situ are likely to be affected by uncertainties from few to several tens of millikelvin, either because of the poor quality of sensors, or for the harsh measurement conditions in which thermometers are employed. Some marine thermometers may deliver in-situ temperature measurements with accuracies within 2 mK, but they need accurate calibration and individual characterization of the influence of pressure on temperature measurements[5].

At the present time, there is no recommendation or guidance describing the best metrological practices that should be employed to realize marine temperature measurements with uncertainties below 2 mK. A close cooperation between metrologists and oceanographers should be started to define procedures and best practices enabling improvement in temperature measurements of seawater.

DEVELOPMENT OF NEW TEMPERATURE SENSORS FOR SEAWATER

The most widely used sensors in marine thermometers are thermistors[2], followed by resistive temperature devices (RTDs). They are widely available worldwide, their technology is well-established, and their metrological characteristics have been extensively studied in the past decades. Their main drawback, mainly in the case of thermistors, is their pressure sensitivity.

They must be conditioned properly in marine equipment, to limit the effect of water pressure on temperature measurements. In addition, they must be aged before use, in order to limit their drift in time within 1 to 2 mK / year, in the best case. Sensor's time-drift may be a limit to measurement accuracy, especially for thermometers mounted on free-drifting profiling floats, where recalibrations are impracticable.

Since few years, research is in progress to develop new temperature sensors based on optical fiber Bragg grating. They look as a possible replacement for RTDs and thermistors in some marine applications: they show insensitivity to pressure and they may require reduced maintenance and recalibrations. They can also be advantageous as distributed temperature sensors, to measure temperature gradient and to detect internal temperature waves in a water column, as they overcome some drawbacks of thermistor chains, notably length limits. Joint actions by the metrology and ocean scientific communities on this topic would be helpful to push such development.

DIRECT MEASUREMENT OF THE THERMODYNAMIC TEMPERATURE

The ITS-90 provides an approximation of the thermodynamic temperature, while reliable seawater thermodynamic models need the knowledge of the thermodynamic temperature, to properly evaluate the energy content of oceans.

Between -2 °C and 35 °C, i.e. the typical extent of marine temperatures, discrepancies between the thermodynamic temperature and the ITS 90 raise up to 4 mK[6]. Corrections can be applied to ITS-90 values to get the corresponding thermodynamic temperature, but they introduce an additional uncertainty up to 1 mK.

The metrological community is developing new systems to perform thermometer calibrations directly in thermodynamic temperature[7], to go beyond the ITS-90. These facilities are essentially conceived for the high-grade standard thermometers used in laboratory, but their technology is getting mature enough to be employed in other systems. Building facilities for the calibration of marine thermometers directly in thermodynamic temperature is a new challenge to allow improved accuracy in seawater temperature measurements and ocean modelling.

3.2 CONDUCTIVITY AND SALINITY

Marc Le Menn, Rajesh Nair

Following the entry into force of the International Thermodynamic Equations of Seawater (TEOS-10), the thermodynamic properties of seawater must be calculated from temperature, absolute pressure and absolute salinity measurements. At this time, absolute salinity can't be measured directly, and is obtained by measuring a practical salinity on the Practical Salinity Scale of 1978 (PSS-78).

A document edited by the WOCE Hydrographic Programme Office in 1991, specified that practical salinity needed to be measured with an accuracy of ± 0.002 and a precision of ± 0.001 to be useful for oceanographic purposes. These requirements have been confirmed recently in a publication by C. Wunsch regarding the monitoring of decadal trends of this parameter. Laboratory salinometers allow measurement uncertainties close to the recommended ± 0.002 for practical salinity. A highly-recognized publication on the metrological needs for climatological key observables has stressed that the calibration and traceability concept of PSS-78 cannot guarantee comparability of the measurement results on this uncertainty level if several years lay between the measurements.

Practical salinity measurements are based on conductance ratio measurements, whereas the seawater conductance value is compared to that of a defined potassium

chloride solution. In contrast, the seawater conductance values could also be referred to the SI.

Since the SI is a stable reference such a route of traceability could overcome long-term incomparability of practical salinity results. However, a key comparison organized by INRiM, under the aegis of the BIPM, has shown that traceability of conductivity measurements, and therefore of the practical salinity measurements, to the SI can be made only with an uncertainty corresponding to 0.007 in terms of practical salinity.[8]

An alternative approach to refer practical salinity to the SI with low uncertainty has been developed in a recent European metrology research project (EMRP-ENV05)[9]. There practical salinity of the most common practical salinity standard (SSW) has been linked to density measurements to link its practical salinity value to the SI, thereby giving long term comparability of practical salinity measurements with uncertainties in the order of at least 0.004. This approach is currently used to verify the practical salinity value of new SSW batches on the basis of an informal agreement between the German national metrology institute and OSIL, the manufacturer of SSW.

However, this loose quality control mechanism might be discontinued at any time due to changes in any of both institutions. Hence, there is a strong need to formalize long term quality control of this most important seawater standard for practical salinity measurements. The same holds even more for the traceability of practical salinity under high pressure, which implications have not been investigated at all up to now. To obtain an estimate for absolute salinity of seawater from practical salinity, the latter must firstly be corrected to give absolute salinity with respect to a reference composition defined in 2008.

In order to account for "salinity anomalies", as is typically the case in marginal seas such as the Baltic Sea, the correction must additionally account for a deviation δSA from the reference salinity. δSA can be estimated by measuring the density of samples of seawater with laboratory equipment, or by measuring the nitrate and silicate concentrations of such samples, the corresponding differences between the Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC), and the associated best estimates of TA and DIC in standard seawater.

For salinity profiles or routine measurements, the TEOS-10 manual recommends using the McDougall et al. (2010) algorithm, which is based on values of silicate concentrations obtained by interpolation of data from a global atlas for this variable established by Gouretski and Koltermann in 2004. While the uncertainty associated with the values used to build the algorithm is only 0.017 g kg^{-1}, it is hard to ascertain the accuracy of the estimates given by it. Another major drawback is that the algorithm is applicable only in the open ocean. Coastal areas are poorly documented as regards to the salinity anomaly since they are subjected to rivers flows and coastal erosion with mixing of fresh water, sediments and alluvium.

New methods of measurement in direct relation with seawater density (from refractive index or speed of sound measurements, by pycnometry) offer novel ways to measure absolute salinity. An experimental refractive index sensor, perfected by a consortium of French institutes and developed by the company, nke Instrumentation, has demonstrated its ability to realize refractive index profiles down to a depth of 2000 m. The resolution of the instrument in terms of the refractive index (< 10^{-6}) corresponds to an absolute salinity resolution of a few mg/kg, which allows the detection of salinity anomalies. But further work is still needed to enhance its response under pressure, and to improve the relations giving the absolute salinity from the refractive index, the temperature and the pressure.

3.3 IN SITU CHLOROPHYLL A FLUORESCENCE

Jukka Seppala

Phytoplankton biomass is a key parameter when estimating the ecological state of sea areas. Information on phytoplankton productivity and biomass is vital when studying the biological responses of coastal seas and oceans to climate change, eutrophication, or any other perturbation. Phytoplankton biomass is often inferred from Chlorophyll a, a dominant pigment for phytoplankton. Chlorophyll a can be measured with various methods. Laboratory methods, based on discrete water sampling and extraction, include chromatographic and spectroscopic ones but they are rather laborious. To obtain cost-efficient information on phytoplankton abundance, at the time and spatial scales of biological phenomena, automated online methods are used, like in situ fluorometry or ocean colour. In situ Chlorophyll a fluorometry is very widely used on ferries, research vessels, gliders, floats and fixed platforms and instruments are available from several manufacturers, based on same measurement principle, but with slightly modified optical setups.

In situ fluorometric Chlorophyll a measurements have been used for decades in detecting the abundance of phytoplankton, but it still suffer from a lack of proper primary calibration materials and protocols. Relatively much attention has been paid to the validation of the fluorescence signal with analytical [Chlorophyll a] measurements using field samples, but without primary calibration even these studies remain unconnected. The most common method is to rely on factory based primary calibration, which is often neither certified nor traceable, and validate fluorescence readings with field samples.

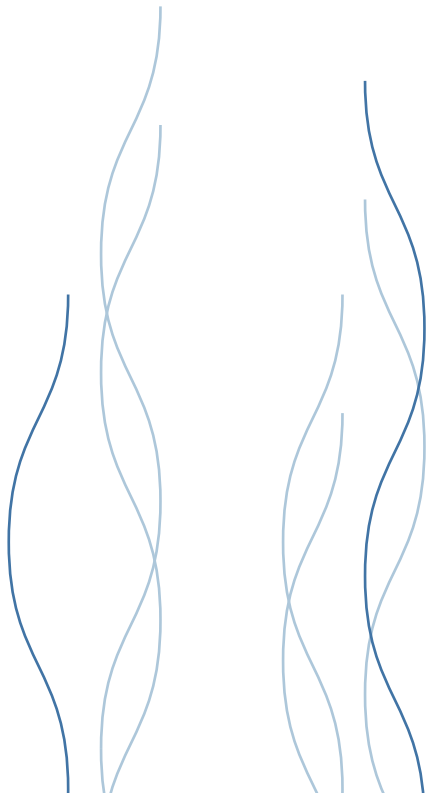
With the current practice the in situ Chlorophyll a fluorescence data from various sources cannot be pooled due to the lack of comparability. This cannot be circumvented using field validation, as methods of validation are not standardized and the amount of validation data is very poor. The way forward would be a consistent and harmonized protocol for fluorometer primary calibration using traceable primary standard resulting in that fluorescence readings are reported in standard units. After such primary calibration the outcomes of various fluorometers may be directly compared and, more, the validation datasets can be shared.

If the primary calibration is done in harmonized way, as proposed here, the fluorescence records will be comparable between instruments, cruises, seasons and operators. This will open possibilities to analyse field validation (relationship between Chlorophyll a fluorescence and concentration) in more detail, when fluorescence data from different sources may be pooled. Eventually this may yield in improved algorithms explaining the variability in Chlorophyll a specific fluorescence and will be a major step forward in analysing the spatio-temporal distribution of phytoplankton biomass and also physiology as requested to better understand e.g. the role of phytoplankton in oceanic carbon cycle.

3.4 OXYGEN

Florence Salvetat

Oxygen is both a key indicator of the quality of water for biological processes and a major parameter for understanding the ocean's role in climate (Joos et al., 2003). Indeed, as oxygen concentrations are very sensitive to physical processes as the airsea fluxes and the interior ocean advection (Karstensen et al. 2008), they play a crucial role in the carbon system of the ocean (Bopp et al., 2002) as well as in the marine nitrogen cycle (Bange et al., 2005). For these two major applications, the requested accuracies are very different: a few tenth of millilitres by litres for the water quality monitoring to a few hundredths of millilitres by litres (or "better than 1 micromole per litre" as it is commonly said) for climatology. In order to reach the latter accuracy (the more critic one), several actions already identified must be conducted by oceanographers together with metrologists and industrials: improvement of reference methods, comparison, definition and dissemination of best calibration practices and mastering and enhancement of sensors technologies.



IMPROVEMENT OF REFERENCE METHODS

Currently, the only method traceable to the Système International d'Unités (SI) is the Winkler titration, an analytical measurement that requires highly skilled operators: the sampling is very sensitive to air oxygen contamination, the preparation of the reagents is crucial for the trueness of the titration and the titration itself is dependent on the adjustment of the device used. All these influent quantities lead to a global uncertainty for the volumetric Winkler estimated around $\pm$ 4 to7 µmol/l, which is far above the climatology target.

In the past, the EMRP Joint Research Project ENV05 "OCEAN: Metrology for ocean salinity and acidity" afforded the opportunity to gather together people from metrology, oceanography and industry and a successful outcome of the project lead to the elaboration and testing of a gravimetric Winkler titration that reduces significantly the uncertainty of the titration (Helm et al. 2012). However, this method suitable for in lab applications can't be applied on board where the major part of the Winkler data is performed. On the basis of what was studied and discussed during the OCEAN project, several stages can be carried out in the next years to improve the quality and traceability of the Winkler dissolved oxygen measurement:

A few laboratories actually master the Winkler analysis and even less the estimation of a realistic associated uncertainty. This first issue need to be addressed urgently through the harmonization of practices and dissemination of knowledge.

Then, a further action will be to work on the automatisation of the sampling and the analysis to reduce as much as possible the influent quantities by improving and developing new methods of detection and devices.

COMPARISON, DEFINITION AND DISSEMINATION OF BEST CALIBRATION PRACTICES

Despite the few laboratory capable of performing dissolved oxygen sensors calibration, several benches have been built all over the world and the full intercomparability of these equipment have not yet been established. As the oxygen community is quite new and small, experiments can be easily carried out to test the existing facilities, status on their pros and cons and finally agree on best calibration practices, including estimation of calibration uncertainties.

MASTERING AND ENHANCEMENT OF SENSORS TECHNOLOGIES

A last but not least topical question to address, is the metrology of sensors. The current practice is the use of optical sensors as substitutes to Winkler analyses, thus strongly increasing the monitoring possibilities. However, despite a large deployment of these kind of sensors, the optical technology is not fully characterized yet. Metrologists from oceanographic institutes need to rely on agreed and recognized protocols to control, calibrate and adjust properly the sensors. These protocols could only be delivered by people skilled in sensor technology, optical detection properties and top level metrology. Once again, the need of collaboration between fields is crucial to the success of the initiative.

3.5 CARBON DIOXIDE

Rajesh Nair,
Maria Filomena G. F. C. Camões

At present, pCO_2 is one of the few directly measurable variables of the seawater carbonate system for which autonomous, in situ sensors, amenable to networking and capable of relaying measurements in real-time or near real-time, are commercially available. More and more, the implementation of such sensors is becoming a predominant feature of environmental and climate-related monitoring activity because of the nature and diversity of the spatial and temporal scales over which observations of the variable needs to be maintained in order to be useful. However, it is rapidly becoming clear that the availability of the technology does not necessarily translate into useful data unless the core requisites of the measuring process, namely, traceability, uncertainty and the grounding of measurements in the institutional frameworks of national metrological agencies, are consistently being taken care of in the most exacting way possible - something notably hard to do, particularly when dealing with field measurements. The last condition is especially important since gathered data can have many uses, including ones with legal, jurisdictional and regulatory ramifications.

Furthermore, to support research, policy and decision-making at a transnational (European) level, the collected data have to be comparable and amenable to fitnessfor-purpose assessments in relation to specific user-group requirements. This will require measurements to be metrologically sound, and instruments to be working within known specifications at all times, even during prolonged deployments in harsh conditions.

The major hurdles to intercomparability include limitations and inconsistencies in the current definitions of the measured variable, the specificities of the seawater matrix, the complexities of operating in the marine environment, variability relating to instrument calibration, and poor metrological rigor in reporting data.

State-of-the-art in-situ sensors currently available for the measurement of pCO_2 in seawater are based either on the equilibration of a carrier gas phase with a seawater sample and subsequent determination of the CO_2 that diffuses through by means of NDIR spectrometry (e.g., the PSI CO_2-Pro, the Contros Hydro-C), on reagent-based colorimetry (e.g. the SAMI-CO_2) or on species-specific solid-state detectors. Optical sensors (optodes) for pCO_2 measurements are also under development (e.g. the Aanderaa model 4797).

Marine pCO_2 sensors are beginning to be deployed more and more in different settings and under diverse conditions in operating contexts that range from straightforward monitoring to pure research. Their use is, however, beset by a number of difficulties of varying importance: insufficient supplies of certified reference material, differences in adopted calibration methodologies, scant operational harmonization, absence of realistic terms of reference for field observations, and poor attention to effective measurement uncertainties. Furthermore, there is no standardized method for the evaluation of the calibration uncertainty of such sensors, and the traceability of the measurements they provide is not currently ensured by NMI-accredited calibration.

There is thus a pressing need to begin building a strong metrological framework for measurements of seawater pCO_2. This will, of course, require linking the principal communities involved, namely, that of the national metrological institutions (NMIs), the oceanographic research institutes and data management entities, instrument manufacturers, and marine data and service providers in general.

Such links will serve to endow similar measurements with the institutional validity required to enhance the effectiveness of Europe's regulatory efforts relating to the marine environment, particularly in relation to climate change, and will help to harness the system of marine observations in Europe for this variable to EU (European Union) policy and development goals both now and in the future.

3.6 SEAWATER pH

Daniela Stoica

Seawater pH is of significant interest to researchers studying the effects of ocean acidification on marine environments. Ocean acidification is a direct response to the increase in antropogenically derived CO_2 in the global oceans.

Over the past decades, due to technical issues, a variety of related but different operationally defined 'pH' quantities have been introduced. However, seawater studies can be particularly problematic for pH for two main reasons; firstly, seawater has a high ionic strength, which causes problems when using conventional pH calibration standards. Secondly, current research in marine science requires an extremely small standard uncertainty in pH measurements (of the order of 0.003), over a fairly narrow range of pH, which is far smaller than the difference between

many of the available operationally defined 'pH' quantities, which may be up to 0.2 pH. To deal with these issues, recently, more and more of the oceanographic community has adopted spectrophotometric techniques (optical method) for measuring seawater pH using an indicator dye. However, the main problem with this technique is that the measurand is not expressed in terms of hydrogen ion activity (classical definition of pH) but in terms of total hydrogen ion concentration (pHT) which creates problems for metrological traceability (different measurands for the same quantity) and the comparability of measurement results.

Inconsistencies between seawater acidity measurements can have a large effect on the characterization of ocean carbonate system (whose state is defined by any two of the four variables pH, pCO_2, total alkalinity and dissolved inorganic carbon). Serious discrepancies, higher than the measurement uncertainties, have been pointed out between measured pH values and calculated ones. The spectrophotometric method for pHT (concentration based concept) has been standardized [ISO 18191:2015: Water quality - Determination of pHT in sea water - Method using the indicator dye m-cresol purple] without offering guarantees concerning data comparability with the other measurands related to acidity, in particular pH (free H+ activity based concept). For this method, a realistic uncertainty budget is missing, thus one of the challenges for seawater acidity measurements would be to assess the components contributing to the combined uncertainty budget of pHT values. Advances in autonomous pH instrumentation now make possible to measure this quantity at moored time-series location. Appropriate (matrix and ionic strength match) certified reference buffer solutions with SI traceability used to calibrate pH sensors are currently missing. Availability of such buffer solutions is necessary to demonstrate the reliability of the sensor and the quality of measured data in relation to fitness-for-purpose.

3.7 NUTRIENTS

Willi Petersen

Determination of nutrients in seawater requires in most cases wet chemical methods as the concentrations are quite low in the micromolar range. Only nitrate can be measured directly by UV absorption but with much less sensitivity (detection limit of 1-2µM) and less uncertainty due to problems of interferences with other substances. However, if the matrix is not changing much (e.g. open ocean water) this method is a reliable in-situ method with very fast response time and can be used in stationary system as well as for profiling systems.

In the lab so called autoanalyser based on continues flow analysis (CFA) are most widely used as they offer a high rate of automatization and high throughput of samples. A detailed description of best practise for nutrient analysis can be found by Hydes et al. [10]. For automated in-situ measurements in the field wet chemical nutrient analyser (e.g. EcoTech NUT, Systea Micromac, WET labs Cycle P) are used. Nevertheless, most nutrient analysis still are performed in the lab. New developments with micro-fluid systems (Lab-on-Chip) are very promising in terms of size, power consumption etc. but not yet at the market.

The measurement principle for nutrients is in most cases based on mixing reagents with seawater and formation of coloured dye with the nutrient compound. The intensity of the colour is proportional to the concentration of the particular nutrient compound in the seawater and can be measured photometrically.

For some nutrients (e.g. ammonia and o-phosphate) fluorometric methods (formation of fluorescent dyes) are also used. A critical point for measuring nitrate is that nitrate can be only measured by previous reduction to nitrite. The reduction is obtained by passing through a cadmium column or by UV-radiation. The efficiency of this reduction step has to be checked regularly.

Ideally nutrient samples should be analysed immediately after sampling to avoid any possibility of biological activity including biofilms in the samples, which will change the concentration of dissolved nutrients. The largest errors in nutrient analysis tend to be due by non-suitable sample containers and by inappropriate storage. In practice samples may be stored (in the dark in cool/refrigerated conditions) for several hours to days. Generally immediate filtering (0.2µ pore size) is recommended to remove particles and bacterial activity before storing. Particular care is required in the case of extremely low concentrations. Such samples can be easily contaminated during sampling and sample storage. Here rapid analysis is advised. For longer storage samples should be frozen as soon as possible after collection. If this is not possible mercury chloride can be used for preservation. Critical can be the analysis of silicate from frozen bottles as silicate tends to polymerise and it takes longer time for de-polymerisation after thawing. Furthermore silica samples should not be stored in glass bottle to avoid silica contamination by glass dissolution.

Both in-situ systems and lab devices need for calibration standard solution of wellknown concentration which should be in the expected concentration range of the later analysed samples. In order to avoid errors by different refractive indexes the ideal matrix for preparation of calibration standards is natural seawater of similar salinity to the samples being measured. However this seawater should contain undetectable or low concentrations of the analytes. Alternatively solutions of high purity grade sodium chloride can be used as artificial seawater (ASW).

The accuracy of the preparation of the standard solutions is critical. To achieve high quality measurements the weighted salts used for preparing standards must be dried. Dilution of primary standards must be done using calibrated pipettes of known reliability. The primary and secondary standards should be made up and diluted into volumetric flasks whose volumes have been checked. The temperature dependency of the volume has to be taken into account. Systems are usually adjusted so that a linear calibration curve can be used to compute sample concentrations. Defined calibration standards should be measured at equally spaced intervals during an analytical run in order to detect drifts variation of the precision. Control chart showing the variation of the precision (standard deviation) of determination are recommended. Automated in-situ systems should measure a reference sample in the same way. However, the standard has to be preserved by chemicals (e.g. mercury chloride) to keep him stable over a longer time.

Reference Material for Nutrients in Seawater (RMNS) is produced in Japan by KANSO CO., LTD.[11]. RMNS helps to improve the consistency of nutrient measurements between different institutes and cruises. Furthermore collaborative test exercises helps to keep data from different labs comparable. In Europe a project called "Quality Assurance of Information for Marine Environmental Monitoring in Europe" (QUASIMEME) was initiated in 1992 in order to make environmental data more comparable with collaborative test exercises. The QUASIMEME scheme continued on subscription basis. Now it is possible for any laboratory worldwide to participate and to verify the laboratory performance for nutrient analysis.

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4.0 WAY FORWARD

The metrological approach represents an established way to implement such traceability. Yet, metrology is rarely discussed in ocean observing circles and in the marine data management community despite its intimate link to sensor performance, data quality and data usability issues. Thus there is a pressing need to begin building a strong metrological framework for oceanographic measurements and making it an integral part of the marine observing and data management worlds.

Meeting this objective will require the commitment of all the principal communities involved, namely, that of the national metrological institutes, the oceanographic research institutes and data management entities, instrument manufacturers, relevant accreditation and standardization bodies, and marine data and service providers in general.

Acknowledging the above issues, the marine calibration community within JERICO project promoted the establishment of a permanent working group for calibration activities, proposing a future strategic plan towards a permanent, pan-European calibration grid to support the activities of marine observatories.

This idea was endorsed by the JPI Oceans Management Board and an action has been initiated aiming to:

- Connect the calibration operators and facilities within EU in an efficient and productive way,
- Standardize and harmonize operations across the European facilities,
- Reduce costs through sharing the existing calibration infrastructures within the network,
- Capacity building through the exchange and transfer of know-how within the network through a series of workshops, seminars and staff exchanges.

The proposed structure is the development of a grid, which will be open to the whole marine community and will include the national metrological institutes and the sensors manufacturers. Although various levels of organisation can be foreseen (for example primary and secondary reference nodes – PRN & SRN), building this grid will require fostering cooperation between people and groups to promote knowledge exchange and training, nurturing consensus on methodologies and procedures, harmonizing standards of operation, achieving Best Practice, and a rational coordination of resources. To accomplish the above, it is important to find an appropriate funding mechanism within EU while a rational roadmap will involve 2 stages. During the first stage the consortium will be set up with actions focusing on documenting of what is in place, identification of PRN and SRN, harmonisation and standardisation activities. In the second stage funding efforts will be concentrated towards strengthening the existing infrastructures considering that although the calibration procedures of Temperature

and Salinity are well defined, there is a dynamic evolution in terms of

biogeochemical sensors.

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