Symposium

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Underpinning the Seawater Science

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Oceanic In Situ Long term O_2 times series : Challenges & Solutions

Global ocean models predict that, for realistic CO_2 emission scenarios, the oceanic oxygen inventory should decrease about 3 times faster than what we would expect solely from the decreased oxygen solubility of warmer temperature. Also the biological pump affects atmospheric CO_2 levels and fuels most heterotrophic activity in the deep ocean. The efficiency of this pump depends on the rate of carbon fixation, export out of the euphotic zone and the depth of maximum respiration rates. Mineralisation of organic matter (OM) in the water column is a key factor for understanding the oceanic carbon cycle and responsible for the OM reaching the sediment layer to be buried or transformed or mineralised at its surface and affects O_2 in situ concentration leading to anaerobic environment (OMZ).
In the context of the ongoing global warming, long term evolution of in situ O_2 is crucial and requires dedicated adapted strategy. The new technology of automated optical O_2 sensor, with the property of providing “little” drift during long term deployment is an opportunity for us to develop a new generation of tools. Nevertheless, it is compulsory to ensure standardised data quality, accuracy and precision, for science purposes and legacy to the database.

Dominique Lefèvre

Centre National de la Recherche, CNRS, France

Dr Dominique Lefèvre is a research scientist of the CNRS (since 1996). Between 1993 and 1996, he was a postdoctoral fellow at School of Ocean Sciences, University of Wales, Bangor, Menai Bridge, UK, working on marine microbial processes (transfer of organic matter, respiration, photosynthesis). Currently working in the biological CO2 fluxes in the whole water column at different time scale (day to year) using in situ field observations, chemical (O2, TCO2) or enzymatic (ETS) approaches and automated sensors (Seabird, Ysi, Aanderaa). He is the project leader for the development of the IODA6000 (In situ Oxygen Dynamics Autosampler) and ALBATROSS mooring line.
He has been involved in over 30 oceanographic cruises, and principal scientist for 5 of them. He is involve since 2007, and PI of the EMSO-Western Ligurian EMSO node and leaders of EMSO France for the CNRS. He was member of the French coastal vessel committee, since 2006 and president from 2018 to 2023. Author or co-authors of 94 reviewed paper, PI of 10 projects for a total funding of 2.1 M€. He has been involved in over 30 oceanographic cruises, and principal scientist for 5 of them.

Brief state of the art in density/absolute salinity measurements of seawater

Salinity is an ECV or Essential Climate Variable. It allows the calculation of the density of seawater, the sea level or the velocity of geostrophic currents. The needs of oceanographers in relation with climate changes are defined since the 80th in terms of accuracy and precision but they are very close to the best measurements that can be made in metrology laboratories at atmospheric pressure.

This presentation briefly reviews the techniques used in the laboratory and the best performance they can achieve and then looks at the challenge of developing instruments for in situ salinity/density measurements. Many techniques based on the measurement of refractive index n have been explored because n is directly related to the density and composition of the medium. However, it has to be measured with a high resolution on a large measurement range and, given the aggressive nature of the marine environment, this poses a number of problems.

However, a number of promising techniques have emerged in recent years, and this presentation summarises them.

Marc Le Menn

Service hydrographique et océanographique de la marine, SHOM, France

He holds a Ph.D degree in electronics from the University of Bretagne Occidentale (UBO), an engineering degree in physics and instrumentation and a master postgraduate degree in physics systems and metrology from the Conservatoire National des Arts et Métiers in Paris. He is currently head of the metrology and oceanographic chemistry department of the French Navy's Hydrographic and Oceanographic Service, which he largely created. This department is the reference laboratory for the Coriolis consortium, which brings together the main players in French oceanography. Since 2000 he has also been a part-time lecturer on the physics and instrumentation master’s course at UBO.

His passion is to bring metrology into all areas of oceanographic measurement and to improve measurement techniques. Temperature, salinity, sea currents or sea level are the quantities where he has been able to make his contribution.

The role of metrology into the value chain of ocean observations

One of the key challenges facing society is the need to prevent and mitigate the impacts of climate change as well as preserve and restore biodiversity while ensuring sustainable economic growth.

Governments and international organisations have to make complex and interdependent decisions to achieve these ambitious goals. These decisions depend on the availability of reliable environmental data and quality-assured information services.

Observations of Essential Climate Variables (ECVs) and Essential Ocean Variables (EOVs) underpin environmental information services by providing the evidence needed to support climate science and better predict future changes. They help scientists assess climate risks, feed forecasting models and can guide policy decisions on mitigation and adaptation measures.

The ocean is an essential natural and economic resource for food security, tourism, transport, climate regulation and the preservation of biodiversity.

Since the industrial revolution, more than a quarter of the carbon dioxide emissions generated by human activities have been absorbed by the oceans, leading to an increase in their acidity and a decrease in the concentration of carbonate ions.

As ocean acidification is a climatic phenomenon, the quality of the expected data must enable long-term trends to be assessed with a high level of confidence.

Metrology makes it possible to obtain robust and reliable data and helps users to judge its suitability for the purpose for which it is intended.

The talk will show some examples of the metrological tools developed to ensure the quality of the ocean observations. For several years, LNE, the French National Metrology Institute, has been developing reference methods for measuring the acidity of seawater, in particular total scale pH (pHT) and total alkalinity (TA). The reference method for pHT has been applied for the characterisation of reference materials according to the ISO 17034 standard. Moreover, the use of reference materials for the organisation of inter-laboratory comparisons will also be shown. Finally, some examples of collaboration between the metrology and the oceanography communities will be presented.

Paola Fisicaro
Laboratoire National de Métrologie et d'Essais, LNE, France

Paola Fisicaro is research director and head of the Chemistry and Biology Division at LNE, the French National Metrology Institute. Paola’s main skills are in metrology in chemistry, applied to support end users to meet the quality measurement requirements needed for the implementation of EU directives and regulation, as well as International policies.

Paola is currently the deputy chair of the inorganic analyses working group of the BIPM Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM-IAWG) and co-chair of the European Metrology Network for Climate and Ocean Observation, in charge of the Ocean observation section.

In-situ Measurement of Seawater Properties

With the establishment of the Thermodynamic Equation of State, TEOS 10, a solid base has been developed to facilitate development of salinity measurement technologies with better long-term stability and SI traceability, required to investigate, e.g., climate change issues. Measuring in-situ properties of seawater poses specific challenges that are related to the dynamics of the processes under investigation and the response of the used instruments on the variation of the measurement conditions in the field. What has been witnessed during the past years was a refinement of analytical and related data processing methods like deep learning. Those methods unfold their full power if the information on the measured data is completed with the associated uncertainty quantifications. Therefore, the classification and integration of all aspects of the measurement process into an overall framework is a challenge that has to be addressed within the upcoming years.

CHRISTOPH WALDMANN
University of Bremen, WMO member

Dr. Christoph Waldmann has been working as a senior scientist at MARUM, University of Bremen, Germany, for over 26 years and is now retired. He is holding a degree in Physics, and did his Ph.D. both at Kiel University, Germany in 1981 and 1985 respectively. His research focusses on optical and acoustical in situ methods for ocean observations and the development of underwater vehicles. Currently, he is the Chair of the IEEE Ocean Engineering Society Standing Committee on Standards and member of the WMO Expert Team on Measurement Uncertainty.

Ab initio calculation of virial coefficients: from noble gases to water

In the past 20 years, several theoretical advances and a steady increase in computational resources enabled the calculation of virial coefficients of noble gases with unprecedented accuracy. In the case of helium, theoretical results are presently more accurate than the best experimental determination by more that one order of magnitude. In this talk, we will briefly review the state-of-the-art of ab initio calculations of the coefficients appearing in the rigorous density expansion of the equation of state, the speed of sound, and the dielectric constant (generalized Clausius–Mossotti equation) of noble gases and we will highlight their importance in primary metrology of temperature and pressure.
Recently, the same approach has been extended to molecules: although in this case, the large number of degrees of freedom prevents attaining the impressive accuracy demonstrated for helium, theoretical results compare favorably with experimental results. We will discuss our results regarding the second and third virial coefficient of water and heavy water, and our recent ab initio calculations of the temperature-dependent molecular polarizability (first dielectric virial coefficient) in fully flexible models of water isotopologues. The prospects for computing the water-air virial coefficients needed for modeling humid air will be discussed.

Giovanni Garberoglio

Fondazione Bruno Kessler-ECT, FBK-ECT, Italy

Giovanni Garberoglio got his degree in Physics at the University of Pisa, Italy, as a Fellow of Scuola Normale Superiore. He moved to the University of Trento, where he got a Ph.D. in Physics specializing in computational physics, including, but not limited to, condensed matter (solid and liquid), biomolecules, and quantum many-body systems. During a post-doctoral experience at the University of Pittsburgh, he became an expert in path-integral Monte Carlo simulations. Since 2007, he has been active in calculations of thermophysical properties of atomic and molecular gases from first principles, and he is presently collaborating with NIST and other metrological institutes in Europe towards the realization of primary standards of pressure and temperature using gas-based approaches. He contributed to the first ab initio calculation of the third virial coefficient of helium with no uncontrolled approximations, demonstrating that this approach esulted in uncertainties much smaller than those of the best experimental determinations. Subsequently, he extended this approach to acoustic and dielectric virial coefficients, of either atomic or molecular systems (hydrogen and water).

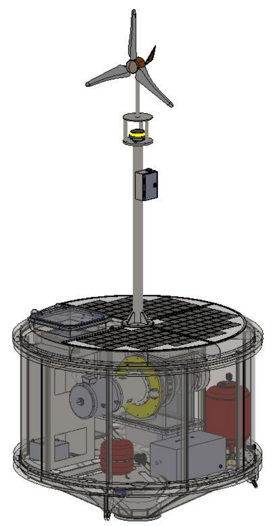
Allan Harvey

National Institute of Standards and Technology, NIST, USA

Allan Harvey received a Ph.D. in Chemical Engineering from the University of California at Berkeley, where he developed equation-of-state models for vapor-liquid equilibria in aqueous systems with electrolytes and dissolved gases. Since 1994, he has been at the National Institute of Standards and Technology in Boulder, Colorado. One focus of his work has been the use of first-principles calculations of thermophysical properties of gases for applications in metrology for temperature, pressure, and humidity, and also to provide gas-phase data for industrial applications such as water content in CO_2 pipeline transport and gas flow metering in semiconductor processing.

From concept definition to full scale prototype of a hybrid wave energy converter to produce fresh water and electricity

The Water Energy Point Absorber (WEPA) is a heaving single-buoy point absorber optimized for a specific site off the west coast of Sardinia Island. It has the main objective of producing electricity and freshwater from desalination, and it has been developed thanks to the experience of Politecnico di Torino and its spin-off company, Wave for Energy Srl in the frame of the project "Waves4Water" sponsored by Parco Naturale Regionale di Porto Conte e Area Marina Protetta Capo Caccia - Isola Piana.



The WEPA architecture is simplified to the maximum extent to increase reliability and reduce maintenance. It integrates a wave energy converter, solar PV and a wind turbine. The goal is to drastically reduce the costs to reach economic sustainability and marketability in the shortest possible time. The working principle of WEPA is efficient and straightforward, it harvests energy from the relative motion between the buoy and the seabed.

The WEPA design and optimization process is based on a simulation tool internally developed. The model requires as input data the hydrodynamic properties of the body and the irregular wave profile obtained from the site-specific statistical data, such as significant wave height and period. The simulation tool uses time-domain mathematical models based on the Cummins equation. It uses Matlab-Simulink environment to solve the ordinary differential equations.

Thanks to the extensive modelling and tecno-economic optimization the final configuration for the case study is identified. Subsequently, the design phase has started, the hydrodynamic modelling of the device exposed to extreme wave climate have provided as outputs the maximum loads and tension to design the mooring system, the hull and the PTO. The final prototype has been built and deployed on the month of June 2023. The testing and data collection of the full scale prototype in currently going on and will provide useful information regarding the behavior in real sea environment.

Marcello Rava
Politecnico di Torino, Italy

On the measurement of the Absolute Salinity of Seawater: state-of-the-art and emerging trends

The Thermodynamic Equation Of Seawater - 2010 (TEOS-10) uses Absolute Salinity SA (mass fraction of salt in seawater) as opposed to Practical Salinity SP (which is essentially a measure of the conductivity of seawater) to describe the salt content of seawater. Ocean salinities now have units of g/kg. SA has the advantage of being a SI unit of concentration, making it a more appropriate quantity to use than SP to obtain the thermodynamic properties of seawater such as density and enthalpy employing TEOS-10. However, despite its fundamental importance, the routine measurement of SA continues to remain a challenge. In this talk, the different techniques currently under investigation for measuring SA will be reviewed, highlighting the latest and most promising developments, and paying particular attention to in situ applications where the need is most pressing.

RAJESH NAIR
Istituto Nazionale di Oceanografia e di Geofisica Sperimentale, OGS, Italy

Rajesh Nair has more than 30 years of experience in Oceanography and the Marine Sciences, with a strong experimental background, extensive field skills, and “hands-on” knowledge of a wide variety of marine instrumentation and measurement realities. As part of the permanent staff of the Centro di Taratura e Metrologia Oceanografica (CTMO), the oceanographic calibration and metrology facility of the Istituto Nazionale di Oceanografia e di Geofisica Sperimentale (National Institute of Oceanography and Applied Geophysics) - OGS in Italy, which he helped set up in 2002, his present activities and interests focus on marine observing technologies, including calibration, control and testing of instrumentation, and the application of metrological principles to marine measurements and data quality assurance both in the laboratory and in the field. Rajesh is actively involved in Ocean Science research at both the Italian national and EU (European Union) levels, and internationally. He is one of Italy’s national representatives in the EU’s JPI Oceans (Joint Programming Initiative - Healthy and Productive Seas and Oceans) European Marine Sensor Calibration Network Joint Action, collaborates actively in the work of IOC-UNESCO’s Ocean Best Practice System (OBPS), and is also currently co-chairing the Technology Panel Working Group (TPWG) of the European Global Ocean Observing System (EuroGOOS), the European component of the Global Ocean Observing System (GOOS).

INRiM activity in the field of metrology for the determination of CO_2 in atmosphere and seawater

Carbon dioxide (CO_2) is one of the main greenhouse gases (GHGs) contributing to global warming. Its concentration has grown continuously reaching a global monthly mean of 420.50 µmol mol-1 in May 2023 [1]. The accurate and sound determination of the atmospheric concentration of GHGs enables the development of models to predict future scenarios and to put into action effective measures to counteract the phenomenon of global warming. The rising levels of CO_2 in atmosphere, highly caused by anthropogenic emissions, are responsible for fundamental changes also in seawater carbonate chemistry. The oceans are absorbing more CO_2 from the atmosphere, which is decreasing seawater pH leading to the acidification of marine waters, with important consequences for the global ecosystem. At present, the partial pressure of CO_2 (pCO_2) is one of the few variables of the marine carbon cycle directly measurable in situ. Despite the availability of a variety of sensors, currently used to monitor pCO_2 in the marine environment, there are several problems to be faced, such as the differences in adopted calibration methodologies and measurement procedures, the lack of metrological traceability for field measurements, the scarcity and expensiveness of suitable reference materials to calibrate the instrumentation. In this framework, it is very useful to have metrological references represented by gas mixtures with CO_2 concentration at atmospheric level, to ensure the reliability of the results and the possibility to compare them internationally. In addition, it is necessary to reach uncertainties small enough to discriminate observed variations due to natural fluctuations from real trends, to achieve meaningful and significant measurement results. In this framework, the development and validation of proper analytical methods and measurement standards is of utmost importance, for both the atmospheric and marine measurements. INRiM activity deals with the exploitation of primary methods, based on gravimetry and dynamic dilution, to prepare reference gas mixtures for environmental pollutants, such as CO_2. INRiM is working to become an official producer of certified reference materials (CRMs) for the amount fraction of CO_2 in matrices of synthetic air or nitrogen, in accordance with the requirements of the ISO standard 17034:2016 [2]. INRiM is also cooperating with other NMIs and Institutions in the framework of Joint Research Projects such as the H2020 MINKE Project "Metrology for Integrated Marine Management and Knowledge-Transfer Network" [3], carrying out feasibility studies to extend the use of the produced primary mixtures to the calibration of pCO_2 sensors, in cooperation with the National Institute of Oceanography and Applied Geophysics (OGS).

References
[1] https://gml.noaa.gov/ccgg/trends/global.html
[2] ISO 17034:2016 "General requirements for the competence of reference material producers", ISO, Geneva, Switzerland
[3] MINKE Project: https://minke.eu/

Francesca Rolle
Istituto Nazionale di Ricerca Metrologica, INRiM, Italy

Francesca Rolle is a chemist and holds a PhD in “Metrology: Measuring Science and Technique”, from Politecnico of Torino, Italy. She is a researcher at the Italian National Metrology Institute (INRiM).

She carries out research activities in the field of metrology in chemistry, in particular concerning environmental pollution, within the INRIM Scientific Division “Applied Metrology and Engineering”. Her main activities are the development of analytical methods for the quantification of gaseous atmospheric pollutants and organic micropollutants in real matrices, the establishment of correct traceability chains and the uncertainty evaluation.

Acoustic thermometry in the atmosphere and the ocean

Besides the metrological interest in the realization of extremely accurate temperature standards based on measurements of speed of sound measurements in monatomic gases, several applications of acoustic thermometry are being pursued which require the precise measurement of speed of sound in humid air or in seawater. In the atmosphere, applications include the thermal characterization of the boundary layer using sonic anemometry as well as correction of the temperature dependence of the refractive index of air in distance measurements with optical interferometry. In the ocean, active and passive methods of acoustic thermometry aim at a precise estimate of the progressive temperature increase driven by climate change. To be effective, these applications rely on models of the dependence of speed of sound on several thermodynamic variables of influence. For humid air, we claim that the relative uncertainty of the model prediction of speed of sound can be reduced below 100 ppm, allowing for acoustic thermometry with accuracy in the order of 0.05 K. Comparison with experimental determinations of speed of sound in humid air with two different methods support this claim.

ROBERTO GAVIOSO
Istituto Nazionale di Ricerca Metrologica, INRiM, Italy

Dr. Roberto Gavioso is a senior research scientist at INRiM with a long term experience in the application of acoustic and microwave techniques to the development of temperature, pressure and humidity standards. His achievements in the field include a low-uncertainty determination of the Boltzmann constant based on a measurement of the speed of sound in helium using a spherical resonator and, as a guest researcher at the National Institute of Standards and Technology (NIST), an experimental determination of the molar polarizability of He which first demonstrated the effectiveness of a primary pressure standard based on the calculated properties of He. He is a member of the Working Group for Contact Thermometry (WG-CTh) of the Consultative Committee on Thermometry (CCT) of the Bureau International des Poids et Mesures (BIPM). He is a Lecturer in Physical Acoustics at the University of Torino.